

IV.C.1e Carbon Aerogels for Hydrogen Storage

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Accomplishments

- High surface area (SA) carbon aerogels (SA $\sim 3,200 \text{ m}^2/\text{g}$) have been prepared through a CO_2 activation process. Activated carbon aerogel (CA) with SA of $\sim 3,200 \text{ m}^2/\text{g}$ exhibited gravimetric density of $\sim 5.3 \text{ wt}\% \text{ H}_2$ at 77 K and 30 bar ($\sim 29.2 \text{ g H}_2/\text{L}$).
- Carbon aerogel with large pore volume (up to $2.7 \text{ cm}^3/\text{g}$) was used as a “nanoscaffold” in the preparation of a CA/ LiBH_4 nanocomposite that exhibited over 8 wt% H_2 desorption and showed a decrease in hydrogen desorption temperature relative to bulk LiBH_4 . Work performed in collaboration with Metal Hydride Center of Excellence (MHCoE) members at HRL Laboratories.

Approach

This effort is focused on the design of new nanostructured carbon-based materials that meet the DOE 2010 targets for on-board vehicle hydrogen storage. CAs are a unique class of porous materials that possess a number of desirable structural features for the storage of hydrogen, including high SAs (over $3,000 \text{ m}^2/\text{g}$), continuous and tunable porosities, and variable densities. In addition, the flexibility associated with CA synthesis allows for the incorporation of modifiers or catalysts into the carbon matrix in order to alter hydrogen sorption enthalpies in these materials. We believe these doped CAs are ideally suited for hydrogen storage since the materials combine the high mass storage capacity of the aerogel with high surface-

to-volume metal nanoparticles that can potentially influence the energetics associated with hydrogen uptake and release (i.e. hydrogen spillover). Since the properties of the doped CAs can be systematically modified (i.e. amount/type of dopant, SA, pore size/volume), novel materials can be fabricated that exhibit enhanced hydrogen storage properties. Optimization of these CA materials for hydrogen storage, however, requires a fundamental understanding of the interaction between molecular hydrogen and the carbon-based sorbent. Therefore, we are also developing advanced nuclear magnetic resonance (NMR) techniques to investigate the mechanisms associated with hydrogen physisorption and chemisorption in these carbon-based materials.

In a parallel effort, we are also designing CA materials as nanoscaffolds for metal hydride systems. Recent work by others has demonstrated that nanostructured metal hydrides show enhanced kinetics for reversible hydrogen storage relative to the bulk materials. This effect is diminished, however, after several hydriding/dehydriding cycles, as the material structure coarsens. Incorporation of the metal hydride into a porous scaffolding material can potentially limit coarsening and, therefore, preserve the enhanced kinetics and improved cycling behavior of the nanostructured metal hydride. Successful implementation of this approach, however, requires the design of nanoporous solids with large accessible pore volumes ($>4 \text{ cm}^3/\text{g}$) to minimize the gravimetric and volumetric capacity penalties associated with the use of the scaffold. CAs are promising candidates for the design of such porous scaffolds due to the large pore volumes and tunable porosity of aerogel materials. This research is a joint effort with HRL Laboratories, a member of the DOE MHCoE. LLNL's efforts have focused on the design of new CA materials that can meet the scaffolding requirements, while metal hydride incorporation into the scaffold and evaluation of the kinetics and cycling performance of these nanocomposites is performed at HRL Laboratories.

Results

- High SA CAs (up to $3,200 \text{ m}^2/\text{g}$) have been prepared through a CO_2 activation process. The increase in SA has been correlated to activation time and temperature as well as the density and morphology of the CA.
- The H_2 gravimetric density in these activated CAs was evaluated over a range of SAs (see Figure 1). Surface excess H_2 adsorption at 77 K varies linearly with Brunauer-Emmett-Teller SA for activated CAs with surface areas up to $\sim 2,500 \text{ m}^2/\text{g}$.

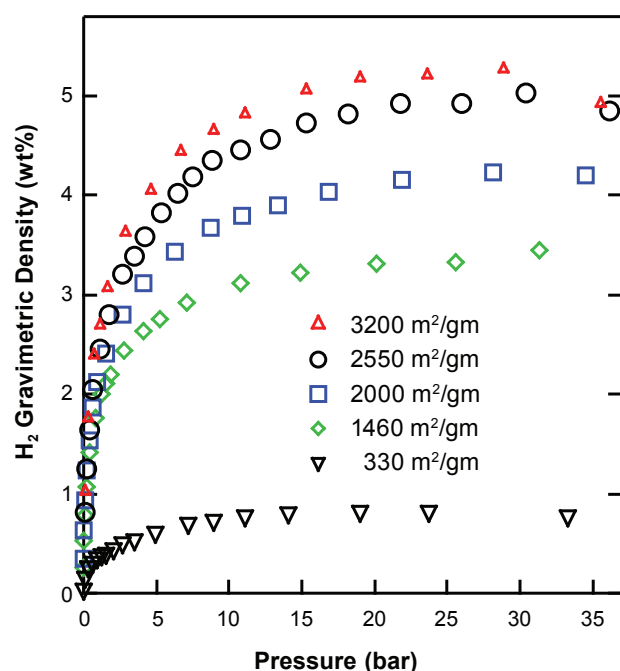


FIGURE 1. Hydrogen Adsorption Isotherms at 77 K for a Series of Activated CAs

H₂ adsorption in higher SA CAs (>2,500 m²/g) exhibited weaker dependence on SA. For example, an activated CA with SA ~3,200 m²/g exhibited a gravimetric density of 5.3 wt% at 77 K and 30 bar (29.2 g H₂/L). Hydrogen adsorption measurements were performed by Hydrogen Sorption CoE members at Caltech.

- CAs doped with Ni and Co nanoparticles showed an increase in the differential enthalpy of adsorption (up to ~7.5 kJ/mol) relative to an equivalent undoped CA material (~6.0 kJ/mol).
- High SA CAs (~2,200 m²/g) containing uniform distributions of Ni and Pt nanoparticles have been prepared through an impregnation process (see Figure 2).
- High pore volume CA scaffolds (~2.7 cm³/g) were used in the preparation of a CA/LiBH₄ nanocomposite that exhibited over 8 wt% H₂ desorption and showed a decrease in hydrogen desorption temperature relative to bulk LiBH₄. Metal hydride incorporation and desorption measurements were performed by MHCoE members at HRL Laboratories.

Conclusion and Future Directions

Based on the promising results from FY 2007, we will continue to optimize the CA microstructure for hydrogen storage. Specifically, we will focus on increasing the microporosity (pore sizes <2 nm) through

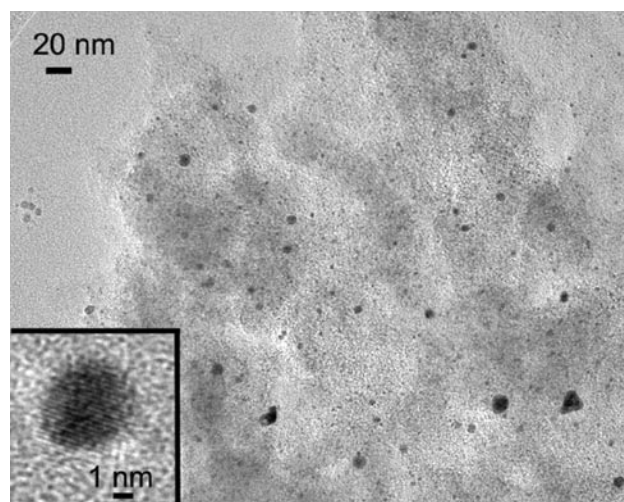


FIGURE 2. Transmission Electron Micrograph of an Activated CA (~2,000 m²/g) Containing a Dispersion of Crystalline Platinum Nanoparticles (Inset Shows a High Resolution Image of a Pt Nanoparticle)

modification of both the synthetic parameters as well as the activation conditions. Such an approach should improve the gravimetric and volumetric capacity of these CA sorbants. In FY 2007, we demonstrated the ability to incorporate catalytic metal nanoparticles (Ni, Pt) into the activated CAs using an impregnation process. We will evaluate the room temperature hydrogen uptake behavior of these metal-doped derivatives to determine the influence that the metal dopants have on the thermodynamics of hydrogen binding in these materials. In addition, we will continue to modify the impregnation process to determine the optimal metal-loading levels, distribution and nanoparticle sizes for enhanced hydrogen sorption. To complement this effort, we are exploring atomic layer deposition as an alternative method for the incorporation of catalytic metals into the activated CA structure. We will also initiate mechanistic studies of hydrogen uptake in these materials using advanced NMR techniques.

For the scaffolding effort, we will focus on the preparation of new CA structures that possess both large pore volumes (up to 4 cm³/g) and small pores sizes (10 nm or less). In our initial studies, a nanocomposite consisting of LiBH₄ in a CA scaffold desorbed ~8 wt% H₂ and showed a decrease in hydrogen desorption temperature relative to bulk LiBH₄. Reversibility in this composite, however, was poor, indicating that the average pore size in this scaffold was not sufficiently small to limit the coarsening of the hydride and the dehydrided products. The flexibility associated with the aerogel synthesis will allow us to design new CA materials with the desired pore volumes and pore diameters. As the CA scaffold structure evolves, our efforts will focus on the homogeneous incorporation of destabilizing agents and catalysts, such as Ni or Ti,

into the scaffold structure to facilitate the hydriding and dehydriding processes. We will also develop methods for controlling the surface chemistry of the CA to improve the wetting behavior of metals, such as Mg, in these materials.

FY 2007 Publications/Presentations

1. H. Kabbour, T. F. Baumann, J. H. Satcher, Jr., A. Saulnier and C. C. Ahn, "Toward New Candidates for Hydrogen Storage: High-Surface-Area Carbon Aerogels," *Chem. Mater.* **2006**, *18*, 6085.
2. T. F. Baumann, J. H. Satcher, Jr., H. Kabbour, A. Saulnier and C. C. Ahn, "Metal-doped Carbon Aerogels for Hydrogen Storage" International Symposium on Materials Issues in Hydrogen Production and Storage, UC-Santa Barbara (August 2006).